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<p>(21) International Application Number: PCT/US98/23194</p> <p>(22) International Filing Date: 2 November 1998 (02.11.98)</p> <p>(30) Priority Data: 60/063,797 31 October 1997 (31.10.97) US</p> <p>(71) Applicant (for all designated States except US): OMD DEVICES LLC [US/US]; 1013 Center Road, Wilmington, DE 19805 (US).</p> <p>(72) Inventors; and (75) Inventors/Applicants (for US only): KOROTEEV, Nicolai I. [RU/RU]; Moscow (RU). MAGNITSKII, Sergei A. [RU/RU]; Moscow (RU). KRIKUNOV, Sergei A. [RU/RU]; Moscow (RU). SHUBIN, Vladimir V. [RU/RU]; Michurinsky Pr. 54-3-143, Moscow, 117192 (RU). MALAKHOV, Dimitry A. [RU/RU]; Moscow (RU). LEVICH, Eugene, V. [IL/US]; Apartment 9L, 330 West 45 Street, New York, NY 10036 (US). MALKIN, Jacob, N. [IL/IL]; Hanavy Havakoukc 13/2, 77461 Ashdod (IL).</p> <p>(74) Agents: COHEN, Herbert et al.; Blank Rome Comisky &amp; McCauley LLP, Wigman, Cohen, Leitner &amp; Myers, Intellectual Property Group, 900 17th Street, N.W., Washington, DC 20006 (US).</p>	<p>(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p> <p><b>Published</b> With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</p>
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(54) Title: MULTI-LAYERED PHOTOCHROMIC OPTICAL DATA DISK

(57) Abstract

A 2.5-dimensional optical storage medium (101) is formed from multiple layers of photochromic molecules embedded in a polymer matrix separated by transparent separating layers (107). The medium (101) is moved into position in three dimensions for two-photon single beam information writing. The information thus written can be read bit-by-bit or page-by-page. In the latter case, an area is illuminated, and the fluorescence is detected by a CCD camera.

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## MULTI-LAYERED PHOTOCHROMIC OPTICAL DATA DISK

Reference to Related Application

The present application claims the benefit of U.S. Provisional Application No.  
5 60/063,797, filed October 31, 1997, whose disclosure is hereby incorporated by reference in  
its entirety into the present disclosure.

Field of the Invention

The present invention is directed to a method and system for use in optical data  
storage systems, such as three-dimensional (3D) optical memories, WORM (write-once,  
10 read-many) drives, and WER (write, erase, and read) drives, and is more particularly directed  
to such a method and system in which a single laser is used to write information on a  
multilayered disk or other medium.

Description of Related Art

One known technique for optical data storage involves two-beam, two-photon writing  
15 and fluorescent reading in a 3D photochromic medium. That technique was developed  
mainly by Peter M. Rentzepis and persons working with him and is described, e.g., in U.S.  
Patents 5,268,862 and 5,325,324 and in the references by him and others listed below.  
Information is recorded with two intersecting beams: a fundamental beam and a second  
harmonic of picosecond YAG:Nd laser radiation. The characteristic pulse duration is about  
20 30 picoseconds, and the pulse energy is several millijoules. That method allows page-by-  
page recording but demands significant modification of existing computer architecture.

Another known technique involves single-photon writing and phase contrast reading  
in multilayered photochromic matrices, photopolymers, and photorefractive crystals. That  
technique was developed mainly by S. Kawata et al and is described, e.g., in the references

by them listed below. That technique has the disadvantages of low spatial resolution and high energy cost.

The following references show the state of the art:

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### Summary of the Invention

In view of the foregoing, it should be apparent that a need still exists in the art for a method and system for optical data storage that offer increased information density at a reasonable energy cost in existing computer systems.

10 It is, therefore, a primary object of the invention to provide a method and system for optical information storage that use a single laser (single wavelength of writing radiation) for writing.

It is another object of the invention to provide such a method and system that provide a simple scheme of information recording.

15 It is another object of the invention to provide such a method and system that use femtosecond (the shortest) laser pulses and achieve high spatial resolution.

It is another object of the invention to provide such a method and system for use with existing computer architecture and in particular with CD-ROM and DVD-ROM standards.

To achieve these and other objects, the present invention is directed to a method and  
20 system for 2.5-dimensional (hereafter known as 2.5D) optical data storage with single-beam, two-photon writing and fluorescent reading from a photochromic medium. The reading may be carried out either sequentially (bit-by-bit) or in parallel (page-by-page). The organic photochromic molecules used in the medium have an initial form A and an excited or colored form B. The molecules are embedded in polymer matrices and have good optical quality,

thereby allowing high spatial resolution, limited only by molecular dimensions. Information can be recorded by two-photon absorption by the photochromic molecules in their initial form A, while the information can be reproduced through the registration of fluorescence emitted by the excited photochromic molecules in their excited form B.

5           The present invention is thus directed to a variant of 3D optical data storage in which the medium is a multilayered photochromic structure such as a multilayered fluorescent disk. The medium has photosensitive layers separated by inert (non-photoactive) polymer layers. That structure allows single-beam, two-photon, bit-by-bit writing whose locality is provided by the small thickness of the photoactive layers and the nonlinearity of the two-photon  
10   process. The multilayered structure provides a 2.5-dimensional optical memory that can be made compatible with existing CD and DVD technology.

          The use of a single beam for recording, rather than dual beams, allows the use of ultrashort light pulses, namely, of femtosecond order. CW mode-locked femtosecond lasers capable of producing femtosecond pulses with a repetition rate of 10 MHz to 10 GHz are  
15   suitable for use in the present invention. Readout can be performed by registration of the fluorescence caused by either single- or two-photon absorption. Single-photon absorption permits page-by-page reading of information.

#### Brief Description of the Drawings

          A preferred embodiment of the present invention will be set forth in detail with  
20   reference to the drawings, in which:

          Fig. 1 is a drawing showing a cross-sectional view of an optical information storage medium according to the preferred embodiment of the present invention;

Figs. 2A and 2B are graphs showing the dependencies of colored form accumulation on the product of pulse energy density and the effective cross section after the effect of several pulses and on the number of pulses;

Fig. 3 shows the dependence of the optimal number of laser pulses for writing one bit of information on the quantum yield of photocoloration and on the required relative form B accumulation;

Fig. 4 is a schematic diagram showing image formation from a multilayer fluorescent matrix during the readout process;

Fig. 5 is a schematic diagram showing a constructed prototype of the present invention;

Fig. 6 is a schematic diagram showing a universal head in writing mode;

Fig. 7 is a schematic diagram showing the universal head in reading mode;

Fig. 8 shows the dependence of the absorption spectrum of a thin polymer film containing naphthacenepyrrodine No. 10 on form B accumulation during the illumination of the medium by blue light;

Fig. 9 shows normalized fluorescence spectra of naphthacenepyrrodine No. 10 in forms A and B;

Fig. 10 shows an image of a pit written by three dots positioned horizontally at distances of about one micrometer, in which the pit dimensions are 1.7 micrometers vertically and 3.7 micrometers horizontally; and

Fig. 11 shows five fluorescent images obtained from five layers of the 2.5D optical medium, the images being recorded directly over one another, the thickness of the photosensitive layers being one micrometer, the layers being separated by distances of thirty micrometers.

### Detailed Description of the Preferred Embodiment

The preferred embodiment will now be set forth in detail with reference to the drawings, in which like elements are designated with like reference numerals throughout.

The storage medium comprises transparent multilayer polymer photochromic matrices which are deposited onto the surface of flat substrates, for example, by a spin-coating method. A cross section of a 2.5D matrix is depicted in Fig.1. As shown in that figure, 2.5D matrix 101 includes a substrate 103 supporting alternating photosensitive layers 105 and separating layers 107. The photosensitive layers 105 can be about 1  $\mu\text{m}$  thick, and the separating layers 107 can be made about 30  $\mu\text{m}$  thick. The photosensitive layers 105 include a polymer in which photochromic molecules are embedded. For example, naphthacenepyridones may be used as the sensitizing photochromic substance. Of course, any other construction can be used as long as the capabilities of the present invention are retained. The separating layers 107 can be made from any transparent polymer or other material. In that context, "transparent" means transparent to the wavelengths that will be used in reading and writing, as will be explained in detail below.

Recording of the information on the medium 101 is based on the photocoloration reaction due to two-photon absorption of strongly focused laser radiation in the photochromic media. The photochromic process used in information recording will now be explained.

Taking into account the typical relaxation times of excited molecular states of complex organic molecules, which lie in the picosecond - nanosecond range, one can see that the time interval between consecutive laser pulses is sufficient for complete depopulation of the excited singlet state of a photochromic molecule. Namely, such excitation is necessary to induce the coloration photoreaction. Thus, the light absorption and the chemical reaction are



separated in time, and, therefore, the processes of light absorption and chemical reactions may be described independently. In the simplest case the two-level model may be used to describe the excitation of photochemical reaction.

Besides that, we will neglect the processes of reverse photochemical reaction, destruction, energy transfer, light absorption by the polymer host and by products of reaction, etc. Let us assume that photoreaction quantum yield is constant. So during light pulse propagation, form A concentration is not changed and after that some part of excited molecules transforms into form B in accordance with quantum yield  $\phi$ , while the rest of molecules returns to the initial state to the moment when the next light pulse comes.

Let us estimate how many molecules are transformed from form A to form B after propagation of  $k$  pulses in assumption that all light pulses are similar and optical density of the media is not large:

$$n_B(k) = n_0 \left\{ 1 - \left[ 1 - \frac{\phi}{2} (1 - \exp(-2\delta \int \Phi^2 dt)) \right]^k \right\}, \quad (1)$$

Here  $\int \Phi^2 dt$  may be determined provided the pulse energy and the pulse temporal profile are known:

$$\frac{\int \Phi^2 dt}{E^2} = \frac{\tau \int_{-\infty}^{\infty} I(t/\tau)^2 d(t/\tau)}{\tau^2 \left[ \int_{-\infty}^{\infty} I(t/\tau) d(t/\tau) \right]^2} = \frac{g}{\tau}, \quad (2)$$

where  $\tau$  is the pulse duration,  $I(t/\tau)$  is the profile of pulse intensity, and  $g$  is form factor. For a Gaussian profile,  $g = 0.664$ , and for  $I(t/\tau) = \text{sech}^2(t/\tau)$   $g = 0.533$ . So (1) may be rewritten as follows:

$$n_B(k) = n_0 \left\{ 1 - \left[ 1 - \frac{\phi}{2} (1 - \exp(-2\delta g \frac{E^2}{\tau})) \right]^k \right\}. \quad (3)$$

Here  $n_B(k)$  is the local concentration of colored form B of photochromic substance after action of  $k$  similar light pulses;  $n_0$  is the total photochromic substance concentration ( $n_0 = n_A + n_B$ );  $n_A$  is the concentration of the initial photochromic substance form A;  $\Phi$  is the local photon flux density during single pulse propagation;  $\delta$  is the two-photon cross section. In these equations the population changes are taken into account. Thus, these equations are valid for any energy in pulses.

The comparison of (3) and the equation for single photon excited photochemical reaction allows to define an effective cross section and to rewrite (3) in the form similar to that equation:

$$n_B(k) = n_0 \left\{ 1 - \left[ 1 - \frac{\Phi}{2} (1 - \exp(-2\sigma_{\text{eff}} E)) \right]^k \right\}, \quad (4)$$

where  $\sigma_{\text{eff}} = \sigma$  in the case of single photon excitation and  $\sigma_{\text{eff}} = \delta g E / \tau$  in the case of two-photon excitation.

After single pulse propagation the concentration of form B is defined as

$$n_B(1) = n_0 \frac{\Phi}{2} [1 - \exp(-2\sigma_{\text{eff}} E)]. \quad (5)$$

If  $2\sigma_{\text{eff}} E \ll 1$  the population change may be neglected and the equation (4) is simplified:

$$n_B(k) = n_0 \left\{ 1 - [1 - \Phi \sigma_{\text{eff}} E]^k \right\}. \quad (6)$$

And in the case of single pulse excited photoreaction

$$(n_B)_s \cong n_0 \Phi \sigma_{\text{eff}} E. \quad (7)$$

If the number of pulses is large, equation (6) may be transformed to exponential form:

$$n_B(k) = n_0 \left\{ 1 - \exp(-\Phi \sigma_{\text{eff}} k E) \right\}. \quad (8)$$

The equation (8) allows to describe the kinetics of photochemical reaction under stationary illumination if a radiation dose  $kE$  is substituted for  $\Phi t$ .

As an example, the characteristics of 3D optical memory device may be estimated.

Let us assume that the average power of femtosecond laser radiation is equal to 15 mW, the

5 pulse repetition rate is 1 GHz (see the disclosure by S.D. Yakubovich et al), the pulse duration is 100 fs, the two-photon cross section of photochromic molecules is  $10^{-47} \text{ cm}^4 \text{ s}$  (that is exactly the value for Rh-6G dye, that may be used for sensitization and 20 times smaller for dye AF-50), the quantum yield of the photoreaction and the form factor are close to 1, and the writing beam diameter is  $0.8 \text{ }\mu\text{m}$  (in accordance with CD standard). Using these

10 parameters we receive  $\sigma_{\text{eff}} \cong 10^{-18} \text{ cm}^2$ . According to the equation (6), after propagation of a single pulse only  $\sim 1\%$  of molecules are transformed into form B. If fluorescence quantum yield of colored form of photochromic substance is rather large, this percentage of accumulated form B is enough to provide reliable reading of information. Thus, the 3D memory device with such parameters is able to write information with a speed as high as 1

15 Gbit/s. The energy expense for writing of one bit of information is equal to 15 pJ (see below).

The energy expense varies inversely as the square root of the pulse duration  $\tau$ , so one should use as short a pulse as possible. Moreover, the shortening of pulse duration permits an increase in the threshold of media optical damage. For  $\tau \sim 100 \text{ fs}$  this threshold in such polymers as PMMA achieves the value of  $\sim 10 \text{ TW/cm}^2$ .

20 Evidently, by using shorter pulses one can record the information by two-photon excitation of photocoloration of photochromic molecules. However, the use of pulses with  $\tau < 50 \text{ fs}$  is connected with specific difficulties because of refractive index dispersion in any medium. So we consider that lasers generating the pulses of 50-100 fs range are most

suitable, i.e. one should use a Ti:sapphire laser, a Cr:LiSAF laser, an Er-doped fiber laser, a semiconductor laser system or a CPM dye laser. We used a Ti:sapphire laser to develop the prototype of 3D optical data storage device.

If the energy of the pulse exceeds the value  $0.5 \sigma_{\text{eff}}$ , the saturation of resonance takes place and the populations of the upper and lower levels become almost equal, then further increasing the pulse energy causes only an insignificant increase in the photoreaction product. The limit of this increase for the first pulse is equal, in accordance with (4), to  $(n_B/n_0)_{\text{max}} = 0.5\phi$ . So, if it is necessary to accumulate the significant amount of colored form and if the quantum yield of coloration is not high enough, it is impossible to record the information bit by single pulse. Increasing the number of writing pulses one can transform the unlimited part of molecules into the colored form as follows from expressions (3,6). The dependencies of relative form B concentration on the effective dose of radiation in pulse after the propagation of one or several laser pulses and on the number of writing pulses for different effective radiation dose in pulse are depicted in Figs. 2A and 2B respectively. One can see that due to resonance saturation of two-photon absorption (Fig.2A), the relative form B concentration limit is defined by number of pulses  $k: (n_B/n_0)_{\text{max}} = 1 - (1 - 0.5 \phi)^k$ . So the further increasing of colored form accumulation may be achieved only by raising of  $k$  (Fig. 2B).

It is worth notice that to take into account the processes of reverse photochemical reaction, the kinetic nonequivalence of photochromic molecules embedded into the polymer host and the resonance energy transfer between excited molecules and non-excited molecules, the real kinetics of the writing process depicted in Figs. 2A and 2B and expressed by equations (3), (4) and (5) will be modified. The modification of relevant equations distortion

may be done by taking into account the quantum yield dependence on relative form B concentration. (The certain experimentally obtained dependencies of quantum yield of photochemical reaction on the relative concentration of form B will be described later.)

One makes efforts for minimizing the energy expenses per one information bit writing  
5 under the development of realistic devices of the rewritable 2.5D optical data storage. The basic photochromic material parameters, digital information density per page, the information writing rate and the sensitivity of readout of information ought to be specified. The simple model developed above of the processes that take place during two-photon writing the digital information into the photochromic data storage media gives the opportunity to estimate the  
10 optimized writing conditions.

Let us introduce the criteria of recording of one bit: the bit is considered to be recorded if minimal detectable form B concentration  $(n_B/n_0)_{\min}$  in the volume restrained by the diffraction limited laser beam focal spot is accumulated.

The task of minimization of energy expenses per one bit cannot be achieved by simple  
15 minimization of the of total energy  $W_s = kES$  (here  $k$  is the number of pulses characterized by the density of energy  $E$  and  $S$  is the pit area) that is necessary to transform the photochromic substance fraction  $(n_B/n_0)_{\min}$  from form A to form B due to non-linearity of two-photon light absorption process. Certainly the value  $W_s$  does not include the important for two-photon writing laser pulse parameters. The analysis of the equations (3) and (4) that describe the  
20 kinetics of form B accumulation under nonlinear two-photon excitation of the photochemical reaction by the train of short laser pulses bring to introduction of dimensionless parameter of “cast energy expenses” per information bit writing. This parameter is defined through the pulse photon flux density  $E$ , the number of pulses  $k$  that are necessary to write one bit of

information, the two-photon absorption cross section  $\delta$ , the pulse duration  $\tau$  and the pulse form-factor  $g$  by following relation:

$$W = kE\sqrt{\frac{\delta g}{\tau}} = k\sqrt{\sigma_{\text{eff}}E}. \quad (9)$$

Thus the minimization of the parameter  $W$  will define the way of the optimization of the two-photon writing.

By solution of the equation (4) with regards the value of  $W$  one may obtain the relation between  $W$  and  $(n_B/n_0)_{\text{min}}$ :

$$W = k\sqrt{\frac{1}{2}\ln\left\{1 - \frac{2}{\varphi}\left[1 - \sqrt{1 - \left(\frac{n_B}{n_0}\right)_{\text{min}}}\right]\right\}^{-1}}, \quad (10)$$

The quantum efficiency of the direct photochemical process  $A \rightarrow B$  that is consequent for the colored form accumulation under two-photon excitation conditions appears as the parameter in last relation.

Obviously the relation (9) describes a non-monotonic function  $W(k)$  that is dependent on the parameter  $\varphi$ , that is, quantum yield of direct photochemical reaction. However, there is no possibility of finding the analytical expression for minimum value of  $W$  for various  $(n_B/n_0)_{\text{min}}$  and  $\varphi$ . To perform the result of calculation of optimal energy expenses per writing one bit of information  $W$  according to (9) in pictorial form we depict in Fig. 3 the curves that define such combinations of  $(n_B/n_0)_{\text{min}}$  and  $\varphi$  that the values of  $W$  are minimal for definite numbers of pulses. Thus the area in coordinates  $(n_B/n_0)_{\text{min}}$  and  $\varphi$  is divided into segments within which the optimum number of writing pulses is defined. Besides that one can mention that according to (6)  $(W/k) = \sqrt{\sigma_{\text{eff}}E}$ . It is evident that the optimum  $W/k$  relation does not

change significantly (see Fig. 2A) and it is consequent to expect that according to (4)  $\sigma_{\text{eff}}E$  for any pulse in optimal recording the information regime would not differ significantly from 0.5. Exact calculations show that  $W/k$  in the optimal recording regime is equal to 0.8 for low levels of quantum yield  $\phi$  and low values of necessary relative accumulation of form B molecules  $(n_B/n_0)_{\text{min}}$  and  $W/k$  has a bias to grow slightly as  $\phi$  and  $(n_B/n_0)_{\text{min}}$  approach the value 1 in the limit. So the Fig. 3 gives us the possibility to define not only the necessary number of pulses but also the value of cast energy expenses for writing one bit of information for various values of  $\phi$  and  $(n_B/n_0)_{\text{min}}$ .

The required laser power  $P$  and pulse repetition rate  $f$  may be easily derived if the information recording rate is given from the known value of cast energy expenses for writing one bit of information obtained from (9) or estimated according to Fig. 3:

$$P = \frac{hc}{\lambda} \frac{\pi d^2}{4} \sqrt{\frac{\tau}{\delta g}} W F, \quad (11)$$

$$f = kF. \quad (12)$$

Here  $d$  is the waist diameter of the focused laser beam and  $\lambda$  is the radiation wavelength in vacuo.

It is worth notice that the most thoroughgoing manner to minimize the necessary laser power is the usage of photochromic materials that are characterized by large values of two-photon absorption cross section. E.g., if a laser with 10 pJ per 100-fs pulse is used, then  $\delta = 10^{-47} \text{ cm}^4 \text{ s}$  is necessary to achieve the efficient cross section  $\sigma_{\text{eff}}$  close to single photon absorption cross section in the case of diffraction limited tightness of light focusing. Thus the saturation of two-photon light absorption takes place. The search of new photochromic

materials may be supplemented by the utilization of sensitizers. Certainly the usage of substances with the highest values of photoisomerization quantum yield is recommended.

The essentials of writing optimization is in definition of the optimal number of laser pulses with given duration and temporal profile in which the writing energy ought to be split to minimize the total energy in whole pulses. In another words we define the cast energy expenses per information bit writing  $W$ , found the optimum number of pulses to write one information bit  $k$  and the optimum energy in single pulse of recording radiation

$E_{\text{opt}} = \frac{W}{k} \sqrt{\frac{\tau}{\delta g}}$ . However if the laser used for recording the information is capable of

generating pulses of energy much less than calculated  $E_{\text{opt}}$ , the required number of pulses to write single a information bit becomes large and the cast energy expense per information bit writing is far from an optimal value. In accordance with (6) in this case the cast energy expenses per information bit writing is growing proportionally to the square root of the required number of pulses:

$$W = k \sqrt{\sigma_{\text{eff}} E} = \sqrt{\frac{k}{\varphi} \left\{ -\ln \left[ 1 - \left( \frac{n_B}{n_0} \right)_{\min} \right] \right\}}.$$

(13)

The record-read-erase processes are characterized by quantum yields of corresponding photochemical reactions. It is worth to note that the value of quantum yield may be varied in the process of photochemical reaction. In the case of polymer matrices the variation of differential quantum yield is caused by: 1) the reverse photochemical reaction; 2) the kinetic non-equivalence of molecules because of inhomogeneity of their interaction with polymer host; 3) the energy transfer between photoisomers in the case of high concentration



of photochromic molecules and 4) the different rates of photoreactions along the film depth due to light absorption in the samples with high optical density.

It is worth notice that to realize WER optical data storage device it is necessary to erase information in a way similar to the information writing (two-photon induced  
5 photochemical bleaching reaction).

Information reading in 2.5D optical memory devices may be performed by the registration of fluorescence excited at single- or two-photon absorption. The single-photon reading allows the use of "page-by-page" (parallel) reading. In both cases the reading process is accompanied by the information erasing due to photobleaching of colored form of  
10 photochromic molecules. Page-by-page reading may be provided by a CCD camera. If the reading beam is directed onto the specimen at the Brewster angle, one can avoid the interference with the reflected light.

Under stationary illumination the solution of equations that define the number of molecules of colored form of the photochromic substance that are erased after illumination of  
15 the sample by the reading radiation with constant photon flux density  $\Phi$  during time  $t$  in the unit volume of the informative layer of the data storage medium and the total number of fluorescent photons emitted from that volume during that time correspondingly can be written as follows:

$$n_B(t) = n_B(0) \exp(-\varphi_B \sigma_B \Phi t), \quad (14)$$

$$20 \quad F(t) = \frac{\varphi_F n_B(0)}{\varphi_B} [1 - \exp(-\varphi_B \sigma_B \Phi t)], \quad (15)$$

where  $n_B(0)$  is the initial colored form concentration,  $\varphi_F$  and  $\varphi_B$  are the fluorescence and bleaching quantum yields correspondingly and  $\sigma_B$  is the light absorption cross section at the reading wavelength of the colored form molecules.

The total number of photons which can be emitted from 1 cm<sup>3</sup> is equal to

$$F_0 = \int_0^{\infty} I_{\text{fl}} dt = \frac{\Phi_{\text{fl}}}{\Phi_{\text{B}}} n_{\text{B}} . \quad (16)$$

Under single-photon excitation of fluorescence, partial erasure of information takes place not only in the layer dedicated for reading but in all layers of the medium. One can see from (16) that the ratio of emitted fluorescent photon number to the number of “erased” molecules met with reverse photoreaction B→A is equal to the ratio of quantum yields (fluorescence and photobleaching). Thus this reading method is intrinsically limited in number of readout cycles.

Every readout system possesses the inherent detection limit defined as the minimum number of photons emitted from unit volume during registration time necessary to detect the presence of colored information pit. Let  $\Delta F_{\text{min}}$  be the minimal number of photons which can be registered by the system to get a distinguishable signal (detection limit). The maximum number of reading cycles  $N_{\text{max}}$  can be estimated for original concentration of form B as integer part of the following expression:

$$N_{\text{max}} = \left[ \frac{\Phi_{\text{fl}} n_{\text{B}} NA}{4\pi\Phi_{\text{B}} \Delta F_{\text{min}}} \right], \quad (17)$$

where NA is the numeric aperture of reading objective.

Evidently to achieve the maximal number of readout cycles one ought to change illumination dose in every readout cycle to provide the constant fluorescent photon numbers in every cycle that is equal to the detection limit. Nevertheless in practice the simplest way is to read the information is to keep the illumination dose constant at every cycle. In this case the maximum number of readout cycles in the single layer is defined by relation:

$$K(F) = \frac{\ln N_{\max} + \ln[1 - \exp(-\varphi_B \sigma_B E)]}{\varphi_B \sigma_B E} + 1. \quad (18)$$

At large  $N_{\max}$  the readout number at optimum reading dose  $E^{\text{opt}}$  is equal approximately to:

$$K_{\max} = \left[ \frac{N_{\max}}{e} \right] + 1,$$

5 (19)

and the optimal readout illumination dose is  $E^{\text{opt}} = eF_0 / N_{\max}$ .

To analyze the influence of other layers' fluorescence during page-by-page reading, it will be assumed that the matrix has  $M$  layers. Assume that integral absorption of reading illumination in all layers with recorded information is small. The information density in a single layer can be characterized by the parameter  $\eta = S_{\text{rec}}/S$ , where  $S_{\text{rec}}$  is the area that was colored during information recording and  $S$  is the total page area. The image contrast  $k$  may be defined as the ratio of difference of signal intensities inside and outside the colored pit to the signal intensity outside the colored pit:  $k = (I_p - I_0)/I_0$ .

Let the definition depth of the objective be much less than the distance between information layers. In this case the fluorescence image formation is depicted in Fig.4. The symbols  $J-1$ ,  $J$ ,  $J+1$  denote the images of three consequent layers of a multilayer matrix formed at a CCD camera having a target plane. The images are formed by a microobjective. It is assumed that the distances between information layers are similar. Light beams forming the pit image are located within the cone defined by the angular objective aperture  $\alpha$ . If the objective magnification is large,  $\alpha$  is approximately equal for all image layers. In Fig.4 the case of the focused image of layer  $J$  on the surface of the CCD

camera 401 disposed at the target plane 403 is represented. Let us recall that all layers are illuminated simultaneously.

Let us calculate the image contrast for pit displaced on the optical axis in the J-layer. According to Fig.4 into the point of pit image besides the radiation emitted exactly from the considered pit comes the collected by objective part of radiation emitted from the area corresponding to the image area S of the neighbor layer and the radiation from other layers of matrix. The image area S is limited by the circle that is the intersection of the cone  $\alpha$  with a vertex in the point of the considered pit image and the plane of the image of the corresponding neighbor layer. Corresponding beams are represented by solid lines 407 in Fig.4. Besides that we shall mention that every pit deposited in the neighbor to reading layer illuminates an area similar to the area S in the plane of CCD camera target (in this case the beams are represented by dashed lines 409 in Fig.4).

Let the pit image be formed by fluorescent radiation of power P. Then the intensity of the pit image is  $I_p = P/S_p$ , where  $S_p$  is the area of a single pit image. The intensity of radiation from this pit at the surface of neighboring layer image is  $S_p/S$  times lower. Hence the intensity of radiation from all neighboring layer pits is  $I_{pn} = \eta I_p$ . Similarly the radiation from the background of neighboring layer (that is from the area that does not contains the colored pits) is  $I_{on} = 1 - \eta I_0$ . According to geometric similarity consideration it is clear that the radiation level from any matrix layer is equal to the considered radiation level of neighboring layer.

Hence the total alias radiation from all layers  $I_{ia}$  on the image plane of the layer J is:

$$I_{ia} = (M - 1) [\eta I_p + (1 - \eta I_0)] . \quad (20)$$

So the contrast of pit image obtained during information reading from the matrix with the M layers is:

$$k_M = \frac{(I_p + I_{ua}) - (I_{ua} + I_o)}{I_{ua} + I_o} = \frac{k}{1 + (M-1)(1 + \eta k)} \quad (21)$$

When  $M=1$ , as it ought to be,  $k_M=k$  and if  $k \rightarrow \infty$  the equation (21) transforms to:

$$k_M \cong \frac{1}{\eta(M-1)} \quad (22)$$

Let us estimate the probability of multilayer matrix readout error. The required noise  
 5 level depends on the method of pattern recognition. Let us assume that two-level coding of  
 information is used and that information recording is provided in such manner that the pit  
 localization at the surface of any layer is known. In this case the signal from every pit can be  
 averaged over the total pixel number ( $n$ ) on the CCD matrix corresponding to one pit of  
 information. The sample size in this case is equal to  $n$ .

10 Let us assume that the intensities of signal and phone are normally distributed values,  
 that the mean values are  $\bar{I}_p$  and  $\bar{I}_o$  correspondingly and that the distribution dispersions of  
 this values are similar and equal to  $\sigma$ .

The definition of phone level and its dispersion may be done over the large area and  
 thus over the large number of CCD pixels. That is why the statistical assurance of the  
 15 definition of these values is much better than the statistical assurance of the signal level  
 definition because the last one is defined by the single information pit area. Besides that we  
 assume high accuracy of signal level determination or the determination of its minimum  
 value.

The information that is contained in the pit volume discrimination criterion under the  
 20 noise presence conditions may be introduced. Let the contrast of information reading be  
 known and equal to  $k_M$ . Thus without taking into account the noise value the pit signal exceed

the phone level by the value  $\Delta I = k_M \bar{I}_0$ . We will instantiate the signal averaged by sample size  $\bar{I}$  the denotations:

$$\begin{cases} "0" & \text{if } \bar{I} < I_{1/2} = I_0 + \frac{\Delta I}{2}; \\ "1" & \text{if } \bar{I} \geq I_{1/2}. \end{cases}$$

(23)

5 Since the values  $\bar{I}_p$ ,  $\bar{I}_0$  and  $\sigma$  are known, the readout error appearance probability is equal to the probability of the fact that the registered signal obtained from the colored pit will be less than  $I_{1/2}$ . That probability is defined by the relation:

$$P(\bar{I}_{"1"} < I_{1/2}) \cong 1 - \Phi\left(\frac{\sqrt{n}}{2\sigma/\Delta I}\right), \quad (24)$$

where  $\Phi(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^x \exp\left(-\frac{t^2}{2}\right) dt = 0.5[1 - \text{erf}(x)]$  is the standard normal distribution function.

10 The probability of readout error appearance when the pit that is not colored during the information recording is equal in its turn to the value similar to defined by expression (24):

$$P(\bar{I}_{"0"} > I_{1/2}) \cong 1 - \Phi\left(\frac{\sqrt{n}}{2\sigma/\Delta I}\right). \quad (25)$$

It is worth to notice that the assumption of similarity of the signal and phone dispersions that was made previously corresponds to the case when the registration system noise is prevails the noise of data storage medium. In principle the inverse situation also may take place if the random non-uniformity of the medium properties are large. One may expect that the relative dispersions of signal and phone inherent to single layer matrix are equal to each other and the signal dispersion is sufficiently greater than the phone dispersion for multilayer matrices. The minimum error rate value in this case would not be achieved when the signal definition criterion (23) is introduced. So this criterion should be changed. But we

believe that the considered case is realistic because the low level signal registration is necessary to enlarge the reading cycles number and because the uniformity of data storage medium is the technological but not principal parameter.

If the information reading is organized in a sequential regime, for example in a device  
5 that is based on mechanics similar to those of a CD or DVD drive, the influence of fluorescence of neighbor layers onto the readout signal contrast become smaller because the intensity of reading laser radiation is tightly focused into the selected informative layer. An additional diminishment of the noise signal from neighbor informative layers may be carried out if two-photon excitation of fluorescence of photocromic molecules in colored form by  
10 femtosecond continuous train of laser pulses will be used.

Information erasing may be performed either by two-photon excited photobleaching to provide spatial localized erasing of the information in the chosen layer of data storage medium or by single-photon excited photobleaching if all information that was recorded into medium should be erased. The first erasure variant is similar to the information recording and  
15 the second variant characterization is already made as the process that accompanies the readout of information.

The prototype of the described above 2.5D optical memory device that has been built is a table-top setup 501 of Fig. 5 having the following basic elements: lasers for recording, erasing and reading of information, optical modulators, universal module for writing and  
20 reading of images, precision 3D positioning stage with polymer photochromic matrix holder and controlling computer (is not depicted on the scheme). The schematic of the setup is represented in Fig. 5.

The recording is performed by radiation of the cw femtosecond Ti:sapphire laser ( $\lambda=800-860$  nm) 503 focused on the chosen photosensitive layer of the multilayer polymer

matrix 505. This laser produces 100-fs pulses with an average power of 150 mW and a repetition rate of 100 MHz. The argon-ion 5.6-W “Innova-316»”laser (“Coherent”) 507 is used for pumping. The recording beam is focused by microscopic objective (x40, N.A.=0.65) 509 supported by a universal head 511 which is also attached to a Princeton Instruments CCD camera 513. The matrix 505 is supported and moved in three dimensions by step drivers 515. The setup 501 is completed by an electrooptic gate 517, an acoustooptic gate 519, and such mirrors 521 as are needed.

The scheme of a universal head in the recording regime is presented in Fig. 6. The recording radiation after the electro-optical gate 517 is collimated by a lens system 601 into a beam filling the significant part of the microscopic objective 509’s aperture and has an appropriate divergence to minimize objective aberrations. Inside the universal (recording and readout) head 511, Ti:sapphire laser radiation is reflected by a dichroic mirror 603 and directed into the microscopic objective 509.

The pulse energy of the recording radiation varies from 10 to 500 pJ per pulse, while the maximum peak power density inside the photochromic layer reaches  $100 \text{ GW/cm}^2$ . The exposure time used for recording a single dot lies in the range of 1-10000  $\mu\text{s}$  corresponding to 100-1000000 pulses in the train. To read the page of information the image of the chosen layer is focused on the matrix of the CCD camera 513 by the same microscopic objective 509 as is used for recording. Fluorescence is excited by the portion of argon-ion laser radiation at wavelength of 514 nm. The schematic of the universal head in such a readout regime is represented in Fig. 7. The radiation is directed onto the specimen from an opposite side through the transparent quartz substrate 701 of the drivers 515 at the Brewster angle. The beam has sufficient diameter to illuminate uniformly the  $120 \times 160\text{-}\mu\text{m}$  page surface.



The universal head 511 is motionless and the choice of the selected layer is provided by 3D specimen displacement. This displacement is carried out with the help of the three step-motors or drivers 515 which drive the precision platen. The accuracy of spatial displacement is 0.22  $\mu\text{m}$  along any coordinate.

5        Writing radiation is dosed by pulse train duration controlled by the electro-optical gate, while the readout time is controlled by the acousto-optical gate.

Specimen displacement, switching of the gates and operation of the CCD camera are computer- controlled.

The storage media specimens are the transparent multilayer polymer photochromic  
10    matrices which are deposited onto the surface of round (20 mm in diameter, 5mm thick) quartz substrates by spin-coating method. The thickness of photosensitive layers is about 1  $\mu\text{m}$  and separating layer thickness is about 30  $\mu\text{m}$ . We use PMMA or its copolymer with polystyrene and acrylonitrile as a host for photosensitive layers. Separating layers were made from polyethylene terephthalate. In this paper we report the results obtained when  
15    naphthacenepyridones (NP) are used as photochromic substance. Most results were obtained with NP No. 10. The main photochemical characteristics such as extinction coefficients of initial and colored forms, fluorescence and photoreactions quantum yields of this substance in toluene solution are represented in the cited paper.

Representative absorption spectra of a thin 1- $\mu\text{m}$  polymer film containing NP No. 10  
20    are depicted in Fig. 8.

One can see that polymer films containing NP are transparent in the near IR spectral region. Thus it is easy to provide two-photon writing into any layer of a 2.5D optical matrix

volume. The form A and B absorption bands in visible spectral range are strongly separated (450 nm and 530 nm). Thus any of these forms may be excited selectively.

Representative normalized fluorescence spectra of both NP No. 10 forms are depicted in Fig. 9.

5           Although fluorescence spectra of two forms of NP No. 10 overlap, the significant difference in positions of the absorption bands of form A and form B and in their fluorescence quantum yields allows one to read the information correctly and efficiently.

One of the sufficient characteristics of 2.5D memory devices is the spatial resolution in the full cycle of recording and readout. The image of an information pit written as three  
10   dots horizontally shifted by  $1\mu\text{m}$  (less than single dot diameter) is depicted in Fig. 10. The transverse dimension of the pit is  $\sim 1.7\mu\text{m}$ , while the longitudinal pit dimension is larger by  $2\mu\text{m}$  (as it is expected to be), i.e.  $\sim 3.7\mu\text{m}$ . So the transverse dimension of the pit is  $0.2\mu\text{m}$  larger than the waist diameter of writing beam. One can expect that the dimension of written pit is to be less than the diameter of the writing beam waist due to the non-linearity of the  
15   two-photon writing process. The observed enlargement of pit dimensions is not the principal limit of storage media but, in our opinion, is connected with the effects of writing process saturation. The saturation level is strongly influenced by photodestruction, reverse photoreaction, light absorption by other levels of molecules, by photoreaction quantum yield change due to inhomogeneity of molecules embedded into polymer host, and so on.

20           The majority of these effects are sufficient not only for the decrease of resolution but also for the rate and energy changes of the recording and the erasure of information. Moreover, these effects have influence on other significant characteristics of optical memory devices such as the achievable number of record-erase cycles.

The theoretical estimations set forth above were made for ideal conditions of recording and readout of information. In order to describe the real processes, more detailed analysis should be done. The influence of reverse photochemical reaction, quantum yield decrease during photoreaction, oxygen effect, and the difference between single- and two-photon absorption spectra should be taken into account. All these factors are able to deteriorate significantly the parameters of recording, reading and erasing the information.

As it has been mentioned above the described setup can be used not only as a pilot prototype of 2.5D optical memory device based on two-photon recording and fluorescent reading of information but also as a photochromic materials tester. Besides the two-photon excitation of photochromic molecules, the non-stationary single photon excitation by femtosecond laser pulses is also interesting and may be investigated with the help of this setup.

The designed setup provides writing, reading and erasing the information according to the principle: two-photon single beam "bit-by-bit" writing and fluorescent "page-by-page" single-photon reading 2.5 D femtosecond optical data storage. Reliable functioning of the 2.5D data storage prototype has been demonstrated via information writing into single-, two-, three- and five layer polymer photochromic naphthacenepyridone matrices.

The choice of NP derivatives was determined by several reasons. Photochromic material used in 3D optical data storage must match several severe requirements. Up to now, a suitable photochromic substance has not been found. NP has high quantum yields of photocoloration and of form B fluorescence and a low thermal bleaching constant. On the other hand, these substances are characterized by high photodestruction quantum yields and low two-photon absorption cross sections. Photobleaching reaction limits the form B accumulation during information recording and the number of readout cycles. Nevertheless,

data storage media based on NP provides successful modeling of 2.5D optical memory device.

The results of writing and reading of graphical images with high plot resolution in five layer optical matrix are depicted in Fig. 11. The deposited photosensitive PMMA layers were about 1- $\mu\text{m}$  thickness, contained 0.1 M of NP and were alternated with 30- $\mu\text{m}$  layers of polyethylene terephthalate. Recording was performed by 50-mW Ti:sapphire laser radiation at a wavelength of 860 nm with exposure time of 1 ms for every dot. To read the information the page was illuminated by  $\sim 100 \text{ mW}/\text{cm}^2$  radiation. The CCD camera image accumulation time was 1 s. Obtained spatial resolution is 1.7  $\mu\text{m}$  and image contrast is about 2. In the described setup readout speed was limited by low reading beam intensity (100  $\mu\text{W}$ ).

The preferred embodiment of the present invention thus incorporates the following features. The photochromic material and appropriate femtosecond laser are selected to provide two-photon writing of the information. The multilayer data storage medium can be made according to Fig.1, and the 2.5D optical data storage device in principle may be similar to the prototype schematics represented in Fig. 3. Those skilled in the art who have reviewed the present disclosure should easily be able to develop the software for encoding the information, controlling the information recording, controlling the readout process performed with the help of CCD camera and for decoding the information.

A multilayered data storage medium according to the preferred embodiment is formed as a matrix containing thin (about 1  $\mu\text{m}$ -thickness) layers of polymer with photochromic molecules embedded into it. An appropriate laser is used to provide two-photon recording and fluorescent reading the information. The setup contains a computer-controlled 3D displacement precision stage with a data storage media holder, gates for the writing and

reading laser beams, micro-objective to focus the writing beam and to transfer the page image during reading of the information onto a CCD camera. Those skilled in the art can easily develop suitable software necessary to control the processes of recording, reading and erasing of information.

5           While a preferred embodiment of the present invention has been set forth in detail above, those skilled in the art who have reviewed the present disclosure will readily appreciate that other embodiments can be realized within the scope of the present invention, such as the following. To enlarge the sensitivity of storage media, one can use molecules that are characterized by large two-photon absorption cross section (for example AF-50) as the  
10   sensitizer of the photocoloration reaction by energy transfer that excites the photocromic molecules in initial form during recording process. To realize the WORM (write once read many) type of 2.5D optical memory, one may use the non-reversible coloration reactions in certain photochromic media (e.g. the coloration of lactone form of organic dyes). A semi-reversible WORM drive may be based on coloration of spyropiranes conjugated with  
15   polymer molecules that are irreversibly colored by photochemical reaction while may be returned to initial form after heating. Therefore, the present invention should be construed as limited only by the appended claims.

We claim:

1. An optical data storage medium comprising:  
a plurality of photosensitive layers, each of the photosensitive layers comprising a  
base material with photochromic molecules embedded in the base material; and  
5 a plurality of separation layers for separating the plurality of photosensitive layers  
from one another.
2. The optical data storage medium of claim 1, wherein the base material comprises a  
polymer.
3. The optical data storage medium of claim 1, wherein the separation layers are  
10 transparent at a wavelength of light at which the photochromic molecules are photochromic.
4. The optical data storage medium of claim 1, wherein the photochromic molecules  
comprise molecules of a naphthacenepyrindone.
5. The optical data storage medium of claim 1, wherein the photochromic molecules  
are selected from the group consisting of spiropyrans, fulgides, thiondigoide colors, and  
15 phenoxynaphthacenequinones.
6. The medium of claim 1, wherein:  
the photosensitive layers are 0.1-1 micrometer in thickness; and  
the separation layers are 1-50 micrometers in thickness.
7. The medium of claim 6, wherein the photosensitive layers are at least twenty in  
20 number.
8. A method of optical data storage comprising:  
providing a three-dimensional matrix of a photochromic material having an optical  
property which changes under two-photon absorption of coherent radiation;

positioning the matrix in three dimensions to position a portion of the matrix at a desired position; and

changing the optical property of the portion of the matrix by irradiating the desired position with the coherent radiation in accordance with information to be stored in the matrix.

5           9. The method of claim 8, wherein the optical property is fluorescence.

10. The method of claim 9, wherein the fluorescence changes in anisotropy.

11. The method of claim 9, further comprising a step of reproducing the information by detecting the fluorescence caused by absorption of reading radiation by products of photoreaction within the portion.

10           12. The method of claim 11, wherein the absorption is two-photon absorption.

13. The method of claim 11, wherein the absorption is one-photon absorption.

14. The method of claim 11, wherein the reading radiation is polarized.

15. The method of claim 14, wherein the step of reproducing comprises detecting a presence or absence of anisotropy of the fluorescence caused by two-photon absorption.

15           16. The method of claim 14, wherein the step of reproducing comprises detecting a positive or negative sign of anisotropy of the fluorescence caused by two-photon absorption.

17. The method of claim 14, wherein the reading radiation has a modulated polarization for single-photon absorption.

18. The method of claim 11, wherein the step of reproducing comprises page-by-page  
20 reading in which a plurality of portions of the medium are illuminated simultaneously and in which fluorescence from the plurality of portions is detected simultaneously.

19. The method of claim 18, wherein the fluorescence from the plurality of portions is detected with a CCD camera.

20. The method of claim 18, wherein the reading radiation is polarized.

22. The method of claim 8, further comprising orienting the photochromic material under a field to orient magnetic dipole moments of molecules in the photochromic material.

23. An apparatus for recording information in photochromic medium, the apparatus comprising:

5 driving means for supporting the medium and for moving the medium in three dimensions such that a portion of the medium is positioned at a desired position in accordance with the information to be recorded;

laser means for emitting coherent radiation capable of changing an optical property of the medium; and

10 modulating means for modulating the coherent radiation in accordance with the information.

24. The apparatus of claim 23, wherein the laser means comprises a femtosecond laser with a pulse duration of substantially 50-100 fs, a repetition rate of substantially 100 MHz, and a wavelength outside a wavelength of absorption and fluorescence of the photochromic  
15 medium.

25. The apparatus of claim 23, wherein the driving means comprises means for moving the medium for multi-layer recording of the information.

26. The apparatus of claim 23, wherein the laser means comprises means for focusing the coherent radiation to form an elliptical volume within the portion of the medium.

20 27. The apparatus of claim 23, wherein the modulating means comprises means for adjusting a duration and intensity of the coherent radiation to control the width of pits in which the information is recorded.



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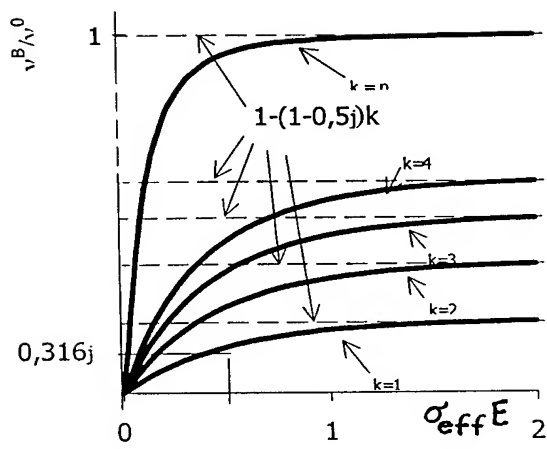
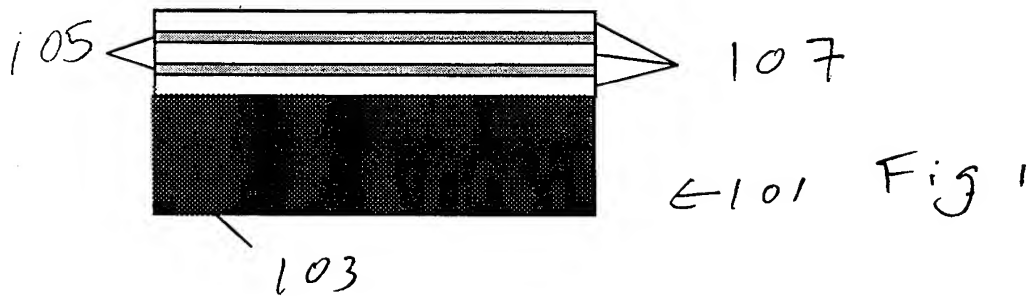


Fig. 2A

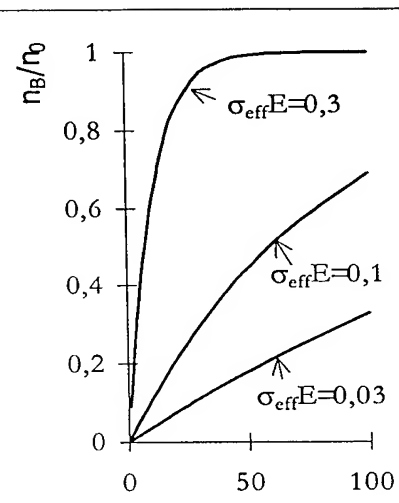


Fig. 2B

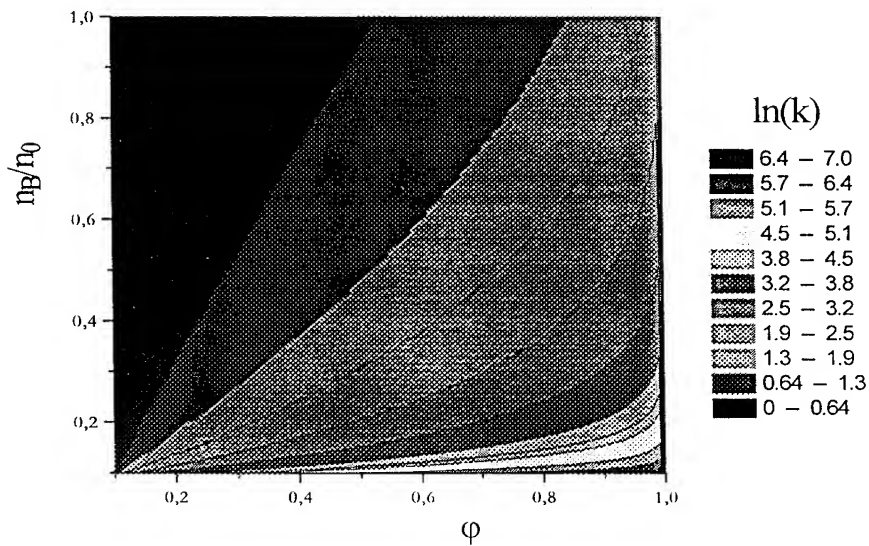
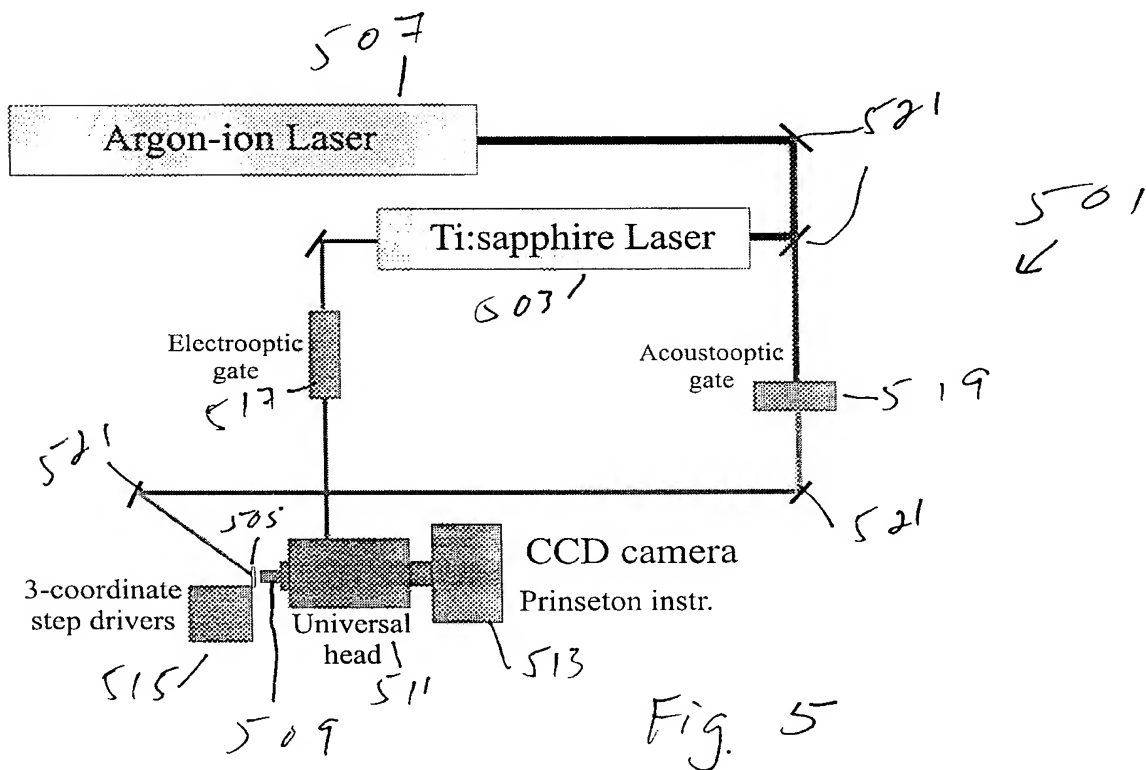
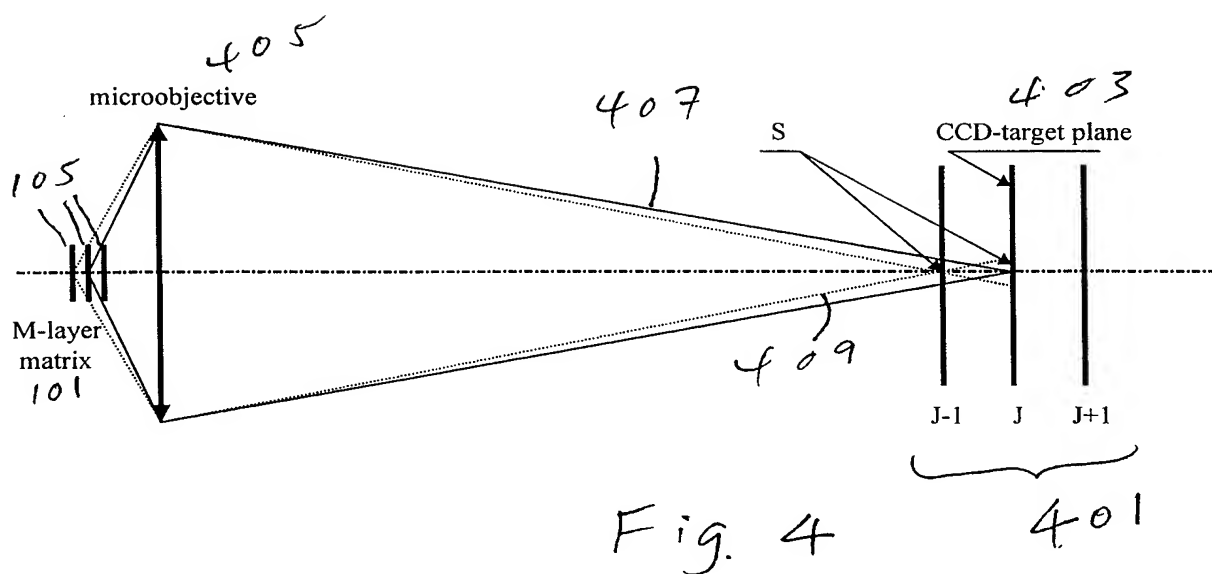


Fig. 3

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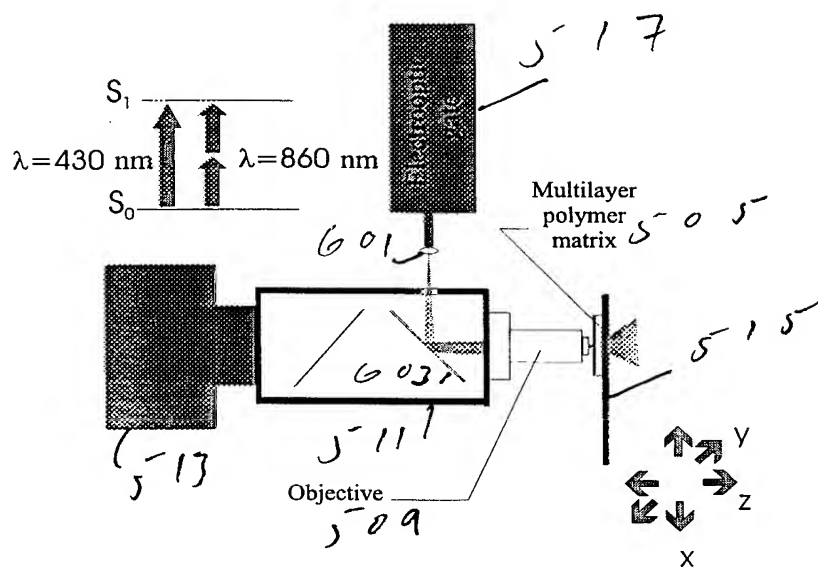


Fig. 6

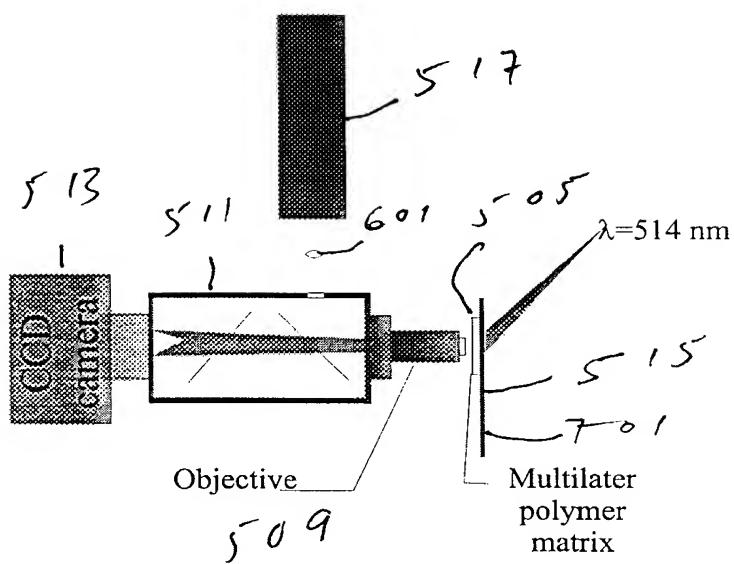


Fig. 7

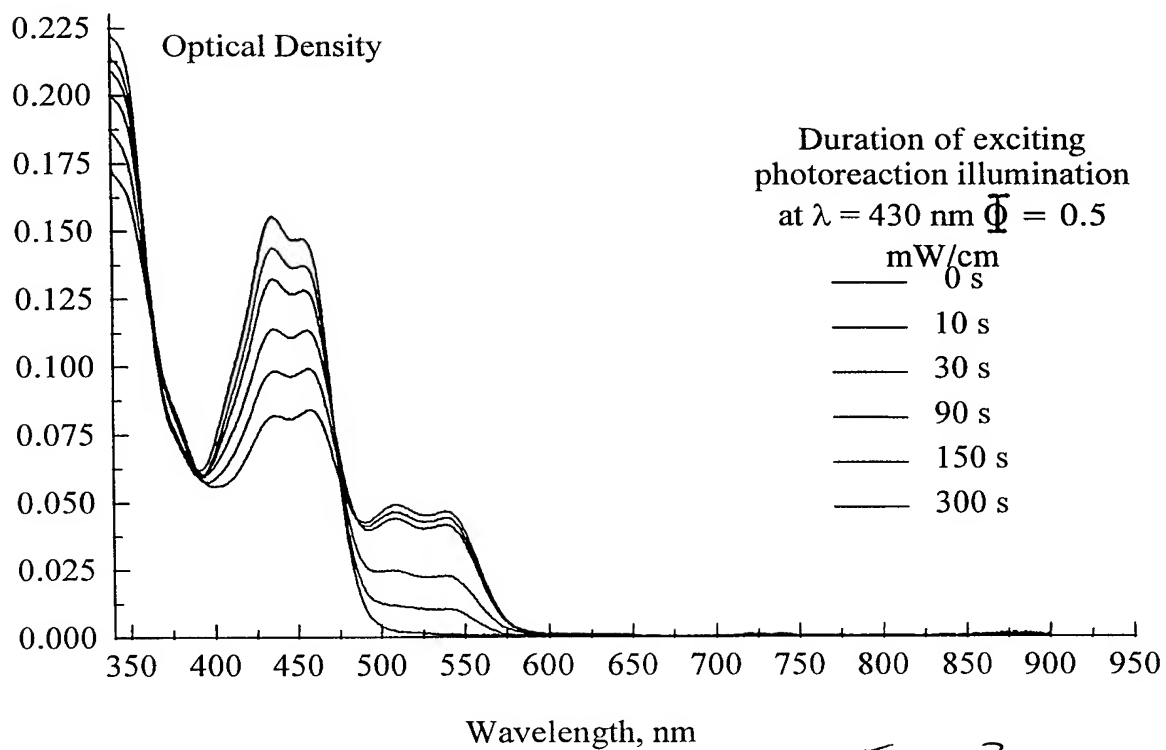


Fig. 8

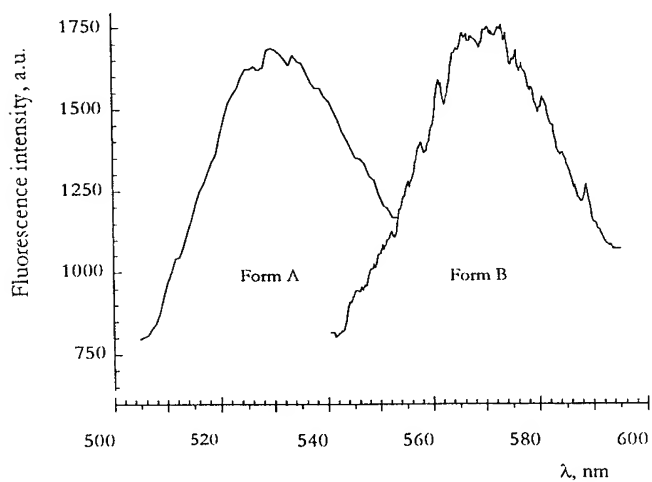


Fig. 9

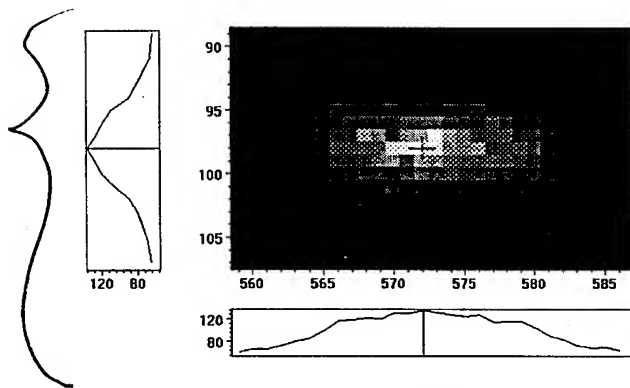


Fig. 10

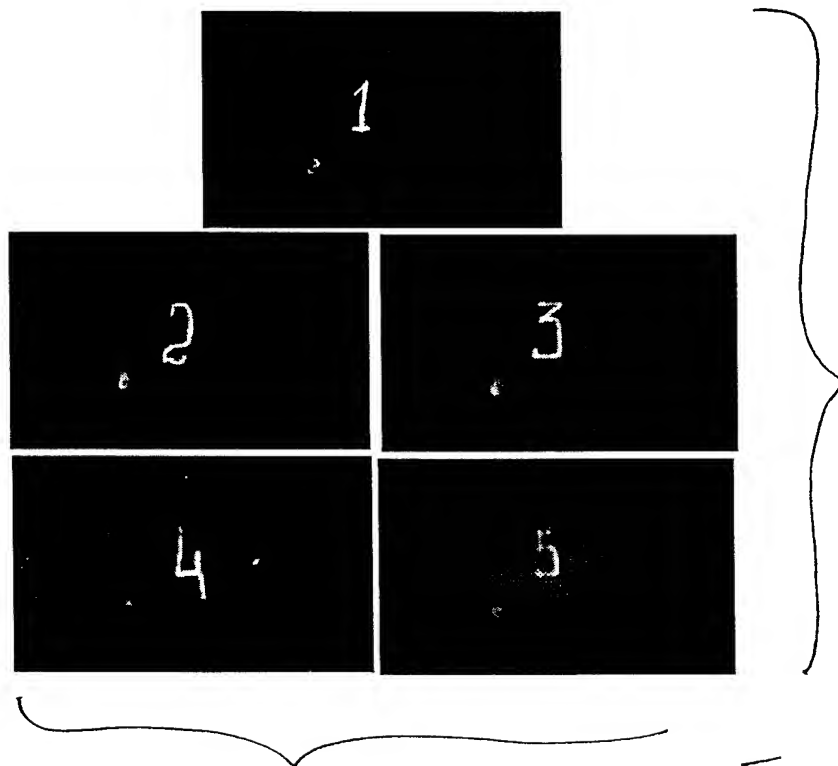


Fig. 11

## INTERNATIONAL SEARCH REPORT

 International application No.  
 PCT/US98/23194

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : G11B 7/24, 3/70; G11C 11/00; B32B 3/00

US CL : 369/283, 284; 428/64.4, 913; 365/151

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 369/283, 284; 428/64.4, 913; 365/151

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS; GPIC 1.0

search terms: disc or disk, optical media or medium, photochromic or photo-chromic, record, reproduce, photon.

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,472,759 A (CHEN et al) 05 December 1995, see entire document.	1-20, 22-27
A	US 5,192,644 A (OHTA et al) 09 March 1993, entire document.	1-20, 22-27
A	US 5,268,862 A (RENTZEPIS) 07 December 1993, see entire document.	1-20, 22-27
A	US 5,325,324 A (RENTZEPIS et al) 28 June 1994, see entire document.	1-20, 22-27



Further documents are listed in the continuation of Box C.



See patent family annex.

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